Measurement of tortuosity of porous Cu using a diffusion diaphragm cell

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Abstract

Open-cell porous metals have many potential applications, such as heat exchangers and flow batteries, due to good permeability for fluid flow. Porous metals manufactured by space holder methods have controllable porous structure, but the fluid pathways and channels are tortuous. The tortuosity can directly influence the fluid permeability and turbulence, which in turn affect the performance of the porous metal. This paper measured the tortuosity of porous Cu, manufactured by Lost Carbonate Sintering (LCS), directly by a diffusion method using a diaphragm cell. The tortuosity of the samples with pore sizes 250-1500 μm and porosities 0.56-0.84 was in the range of 1.33-1.78. It decreased with porosity and increased with pore size. The measured values were comparable to those reported in literature, obtained by the acoustic absorption method.

Key words: Lost carbonate sintering; porous copper; tortuosity; diffusion

1. Introduction

In the last few decades, porous metals have attracted considerable attention in both academia and industry, because of their unique mechanical, thermal and chemical properties [1-3]. Open-cell porous metals, in particular, have many potential applications involving fluids such as heat exchangers [4,5], porous electrodes for batteries [6,7] and wastewater treatment [8], because they have high effective surface area [9] and good fluid permeability [4,5].

Tortuosity of a porous medium characterizes the convoluted pathways, or channels, formed by pores through the porous medium. It is defined as the ratio of the average length of pathways between two points to the straight-line distance between the points in the porous medium [10]. A large tortuosity is caused by the decreased area of available cross-section and

increased path length [11]. Tortuosity is an important property of porous metals influencing fluid related behaviour, including diffusion [11], permeability [12] and dynamic specific surface area [13].

X-ray computed tomography (CT) and acoustic absorption methods are commonly used to measure the tortuosity of porous media. X-ray CT scan can generate a 3D image from a large series of 2D radiographic images and the tortuosity can be calculated from the 3D image [14]. The pathways in the porous metals manufactured by the space-holder methods, however, involves both primary and secondary pores, the latter of which are difficult to be detected by X-ray CT. As a result, the X-ray CT method can lead to significant errors in the measurements. The acoustic method is an indirect method for the estimation of the tortuosity from the acoustic absorption curves of the porous medium [15-18]. It is based on the movement of air in the pathways in the porous medium. Because gases can access pathways that liquids cannot flow through, the acoustically estimated tortuosity is not always useful for porous media intended for applications involving fluid flow. The diffusion method is a direct method for measuring tortuosity, because the tortuosity is the ratio of the average pore length for the major flow or diffusion pathway to the length of the porous medium along flow or diffusion axis [10].

This paper carried out direct measurements of the tortuosity of porous Cu samples manufactured by the Lost Carbonate Sintering (LCS) process using a diaphragm cell based on the diffusion of NaCl in water through the porous structure.

2. Experimental

Porous Cu samples with different porosities (0.55-0.85) and pore sizes (250-425 μm, 425-710 μm, 710-1000 μm and 1000-1500 μm) were manufactured by the LCS process via the dissolution route. The details of the manufacturing process were reported elsewhere [19,20]. The samples were cut into circular discs of 48 mm in diameter and 10 mm in thickness by an EDM machine (WMT ONA E250), with a precision better than 0.1 mm. Before tortuosity measurements, the samples were cleaned in 10% HCl solution and then soaked in distilled water in order to obtain a clean surface and to ensure that water penetrates all pores or channels.

Fig. 1 shows a schematic diagram of the purpose-built diaphragm cell used for the tortuosity measurement, based on the diffusion of NaCl in water through the porous Cu sample. It consisted of two compartments, with the top compartment initially filled with pure distilled water and the bottom compartment initially filled with 1.75 mol/L NaCl aqueous solution. The circular porous Cu sample sat in the middle of the cell between the two compartments. The circumferential side of the sample was sealed by PTFE and PVA tapes, so that the solute (NaCl) can only diffuse through the porous Cu sample from the bottom compartment to the top compartment. To minimise the concentration difference within the top and bottom compartments, the two compartments were stirred by two stirrers at 60 rpm using two rotating magnets placed outside the two ends of the cell. Two pieces of No.1 Filter paper were used to cover both sides of the porous Cu sample to prevent forced flow within the sample due to stirring in the compartments.

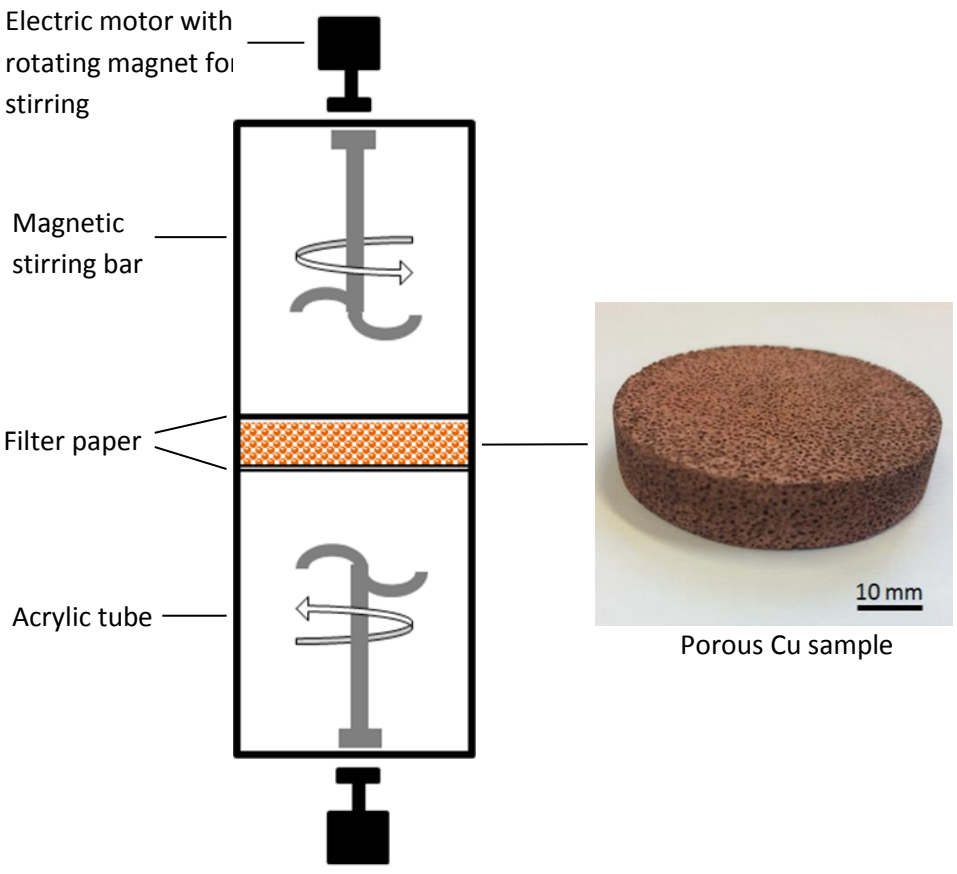

Fig. 1 Schematic of the diaphragm cell used in the tortuosity measurement and a photograph showing a typical porous Cu sample.

The tortuosity of the porous sample can be obtained from the effective diffusion coefficient measured by the diaphragm cell, with respect to the standard diffusion coefficient [11]:

$$\tau = \sqrt{\frac{D_e}{D_o}} \quad (1)$$

where D_e is the effective diffusion coefficient and D_o is standard diffusion coefficient of NaCl in water. The effective diffusion coefficient of NaCl in water through the porous Cu sample can be determined by [21]:

$$D_e = \frac{l}{A\varepsilon(\frac{1}{V_t}+\frac{1}{V_b})t}\ln[\frac{c_{b,i}-c_{t,i}}{c_{b,t}-c_{t,t}}] \quad (2)$$

where D_e is the effective diffusion coefficient; l, A and ε are the thickness, cross-sectional area and porosity of the porous sample, respectively; V is the volume of the compartment; c is the solute concentration in the compartment; and t is the time duration between the initial and final measurements of the solute concentrations in the two compartments. The first subscripts b and t designate bottom and top compartments, and the second subscripts i and t designate the initial and final measurements, respectively.

The diffusion experiment was conducted in an incubator (Thermo Scientific, USA) at a constant temperature of 25 °C for 72 hours. The concentration of the solution in either of the two compartments after the diffusion experiment was measured by quantifying the amount of solute in the solution. This was achieved by heating 50 ml of the solution in a furnace at 220°C to evaporate the water and crystallise the NaCl. Specifically, the solution was poured into a small beaker contained in a large beaker, which was then covered with a lid and placed in the furnace to prevent any loss of solute through splashing and ensure that all of the solute remained in the two-beaker cell. The weight of the crystallised NaCl was measured by an electronic balance, from which the molar concentration of the solution was obtained.

For calibration purposes, an experiment was carried out with no sample between the two compartments. An acrylic tube, 50 mm inner diameter and 10 mm length, both sides covered with two pieces of No.1 Filter paper, was used instead to effect a straight channel. The effective diffusion coefficient under this condition was measured to be 1.474×10^{-5} cm^2/s ($\pm0.03\times10^{-5}$ cm^2/s), which is very close to the standard diffusion coefficient of NaCl in water (1.481×10^{-5} cm^2/s) [20], confirming the validity of the experimental setup. The errors of the

tortuosity measurements were estimated to be around 2.5% to 4.7%, based on the analysis of propagation of uncertainty [22].

3. Results and Discussion

Fig. 2 shows the measured values of tortuosity as a function of porosity and pore size. In the porosity range 0.56-0.84 and pore size range 250-1500 μm, the tortuosity measured by the diffusion method is in the range of 1.33-1.78. These values are somewhat lower than the values obtained by the acoustic absorption method (1.36-2.42) for LCS porous Cu with approximately same pore size and porosity ranges [12]. The difference is likely due to the different fluids used in these two methods. The LCS porous Cu contains secondary pores, which can be easily accessed by air but more difficult by liquids.

Fig. 2 shows that the tortuosity of the porous Cu samples increased with pore size and decreased with porosity and a linear relationship exists between tortuosity and porosity for samples with the same pore size. The results agreed well with a correlation between tortuosity and porosity developed for porous materials with a porosity range from 0.5 to 1 by solving the flow equations using the Lattice Gas Automata method [23]:

$$\tau = p(1-\varepsilon) + 1 \tag{3}$$

where τ is tortuosity, p is a fitting parameter and ε is porosity.

Fig. 3 shows the values of the fitting parameter, p, obtained by fitting the experimental results to Eqn. 3, as a function of pore size. It is shown that the fitting parameter increased nearly linearly with pore size. In other words, the tortuosity increases with pore size and it decreases more rapidly with increasing porosity for samples with a large pore size.

The effects of porosity and pore size on tortuosity can be explained by the distinctive structure of the LCS porous metals. The number of windows connecting the primary pores in LCS porous metals is determined by the number of contacts between the pore former particles, i.e., K_2CO_3 particles, which decreases with pore size and porosity [4]. A smaller number of windows means longer channels for fluid flow through the porous metal, leading to increased tortuosity.

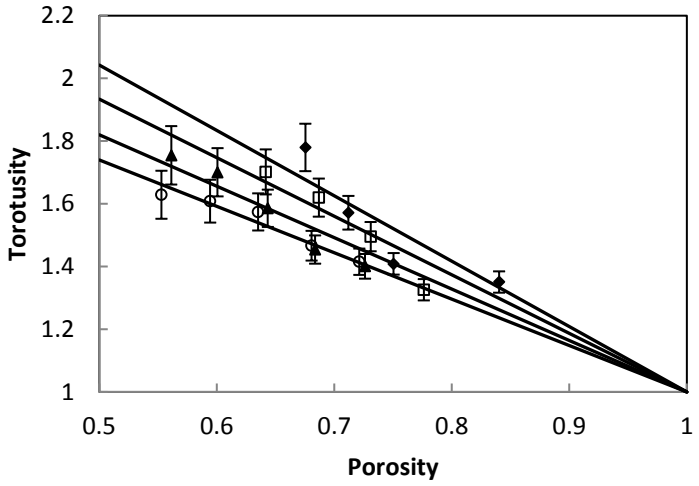

Fig. 2 Variations of tortuosity with porosity for samples with different pore sizes: (○250-425 μm, ▲425-710 μm, ▫710-1000 μm, ◆1000-1500 μm).

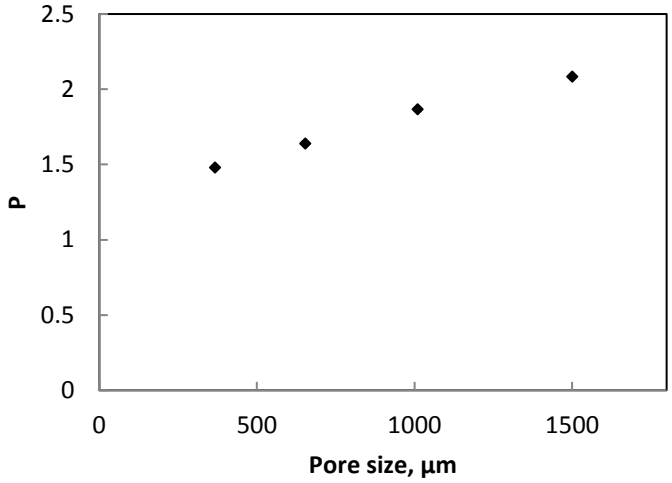

Fig. 3 Variation of fitting parameter, *p*, with pore size.

Conclusions

A diaphragm cell method based on the diffusion of NaCl has been developed and used to measure the tortuosity of porous Cu samples. The tortuosity of the LCS porous Cu samples with different pore sizes (250-1500 μm) and porosities (0.56-0.84) was in the range of 1.33-1.78. The tortuosity decreased with porosity and increased with pore size. The relationship between tortuosity and porosity was found to be in agreement with the correlation reported by Koponen et al[23].

Acknowledgments

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